

IODINE-INITIATED ADDITION OF ALKOXY GROUPS TO A DOUBLE BOND.
ONE-STEP SYNTHESIS OF p-METHOXY SUBSTITUTED α,α' -DIALKOXYBIBENZYLs AND 2,3-DI-PHENYLDIOXANES FROM STILBENE DERIVATIVES.

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(Received in UK 1 November 1971; accepted for publication 18 November 1971)

It has been shown that the iodine-catalyzed isomerization of 4-methoxy- and 4,4'-dimethoxy-cis-stilbene in CCl_4 , CHCl_3 or AcOH at room temperature proceeds via an ionic mechanism¹. We found that the intermediate carbonium ion, formed by addition of a positive iodine ion to the olefinic bond, can be captured in more nucleophilic solvents like alcohols. It appears that such a procedure gives a very simple preparative method for α,α' -dialkoxybibenzyls.

1 g of 4-methoxy-cis-stilbene (cM) and 5 g of iodine are dissolved in 30 ml of methanol. After 24 hours the mixture is diluted with 300 ml of water leaving a strongly acidic solution (pH~1). Iodine is removed by addition of an excess of sodium sulphite and the residual solution is extracted with CCl_4 . After evaporation of the solvent $\alpha,\alpha',4$ -trimethoxybibenzyl is left as an oily product; NMR (CDCl_3 , TMS): τ =6.76 (3H,s) and 6.77 (3H,s); 6.16 (3H,s); 5.83 (1H,d, J=8 cps) and 5.11 (1H,d, J=8 cps); 3.0 (9H,m). The product is free of cis or trans stilbene, the yield is virtually 100%. Starting with the trans isomer (tM), a similar result is obtained.

The NMR spectrum indicates the presence of only one diastereoisomer in the product, probably the erythro compound on account of the rather large coupling constants of the methine protons.

The stoichiometry of the overall-reaction,

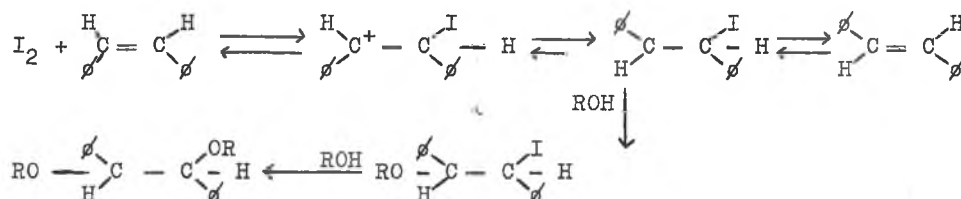


was proved by interrupting the conversion halfway, titration of hydrogen iodide and weighing of the amounts of addition product formed and stilbene left after separation by crystallisation.

By the same procedure 4,4'-dimethoxy-cis- or trans-stilbene (cMM or tMM) could be converted into $\alpha,\alpha',4,4'$ -tetramethoxybibenzyl, but the yield was about 50% and the product had to be separated from tMM by two crystallisations from methanol. Its melting point 141-142° should point out the meso configuration (lit.² meso: m.p. 143.5-144.5°; dl: m.p. 113°). NMR (CDCl_3 , TMS): τ =6.90 (6H,s); 6.25 (6H,s); 5.79 (2H,s); 3.1 (8H,m).

With cMM and iodine in ethanol, even after long reaction times (up to one week), only 18% of a diastereoisomer of α,α' -diethoxy-4,4'-dimethoxybibenzyl was obtained in pure form; m.p. 92.5-93.5°; NMR (CDCl₃, TMS): τ =9.02 (6H,t); 6.76 (4H,m); 6.24 (6H,s); 5.76 (2H,s); 3.0 (8H,m).

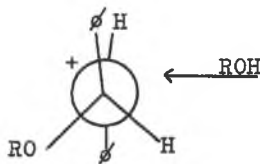
The following reaction scheme accounts for the observed facts:



Iodine dissociates heterolytically as described for the isomerization reaction. The positive iodide ion adds to the double bond. The carbonium ion rotates quickly and can form either the trans-stilbene derivative or react with (m)ethanol.

The next step will be a fast substitution of I by OR. The reaction will probably be of the S_N1 type, because of the good leaving group properties of the I⁻ ion, the polar solvent and the stable carbonium ion formed as an intermediate.

The ROH group will approach the carbonium ion from the least hindered side so that the most stable configuration (meso or erythro)-dialkoxybibenzyl is formed as reaction product.



With glycol instead of methanol or ethanol as the solvent and using rather long reaction times cMM could be converted into 2-phenyl-3-p-anisyl-dioxan; m.p. 61-63°; yield 37%; NMR (CDCl₃, TMS): τ =6.29 (3H,s); 6.24 (4H,s), 5.84 (1H,d, J=5 cps); 4.52 (1H,d, J=5 cps); 3.0 (9H,m); whereas cMM yielded 2,3-di-p-anisyl-dioxan; m.p. 107-108°, yield 50%; NMR (CDCl₃, TMS): τ =6.28 (6H,s); 6.24 (4H, multiplet at high resolution); 5.89 (1H,d, J=5 cps); 4.56 (1H,d, J=5 cps); 3.0 (8H,m). The latter compound differs from 2,3-di-p-anisyl-dioxan (m.p. 79-80°) obtained by Summerbell^{3,4}.

The NMR spectra of the dioxanes show a large difference in chemical shift for the methine protons at C₂ and C₃. These products have therefore probably a rigid structure with axial and equatorial protons.

This is consistent with cis-di-p-anisyl dioxane in the chair conformation.

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REACTIVITY OF DIALKENYLOXYMETHYL CARBOXYLATES TOWARDS CARBOXYLIC ACIDS
A SYNTHESIS OF ISOPROPENYL FORMATE AND OF ACYLAIS

by

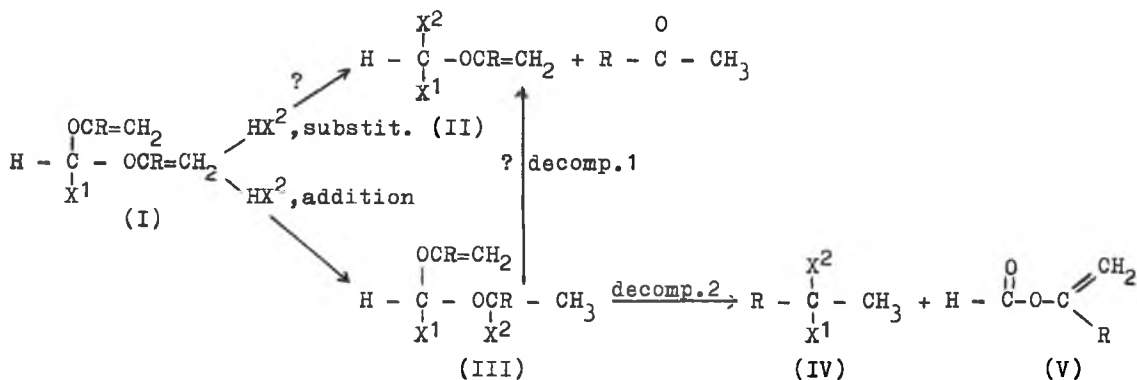
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(Received in UK 27 April 1971; accepted in UK for publication 5 May 1971)

Investigating the reactivity of dialkenyloxymethyl carboxylates, obtained from alkenyl orthoformates and carboxylic acids¹, we found a rather simple procedure for the preparation of isopropenyl formate, which seems ready for further generalization.

In the scheme two possibilities for the conversion of dialkenyloxymethyl carboxylates (I) with carboxylic acids have been given.



R=H or Me; X¹, X²=COOH, COCH₃, COCH₂Cl, COCCl₃

Our experiments clearly indicated that the reaction proceeds mainly via the addition step followed by a fast decomposition of III according to the second pathway; diacyloxy ethers (II) were only incidentally isolated in very small amounts.

In the synthetic procedure a carboxylic acid (HX²) is added dropwise to a

dialkenyloxymethyl carboxylate (I) at room temperature. Only with acetic acid the temperature of the reaction mixture had to be raised to about 80°C. The alkenyl formate (V) is immediately removed from the reaction mixture at low pressure and collected in a dry ice cooled vessel. The highest yields (75%) were obtained with the high boiling mono- or trichloroacetic acid from which it could be rapidly and completely separated. Isopropenyl formate decomposes into acetone and carbon monoxide in the presence of acids. Preparation from propyn and formic acid must be therefore very difficult, which might explain its absence in the literature.

Isopropenyl formate, bp. 80-81°C, $n_D^{20}=1.3990$, was identified by NMR measurements: $\delta = 1.88$, 4.61 and 7.92 ppm relative to TMS intern (~10% solution in CCl_4) for the methyl, the methylene and the formyl proton, respectively. The mass spectrum showed peaks at $m/e = 86$, 58 and 43.

Acylals (IV) are obtained as second products from the reaction mixtures. Ketone acylals ($R=Me$), even with different acid residues ($X^1 \neq X^2$), have not been described before. They could be isolated in yields from 50-80% (see table I) and have been identified after distillation through a vigreux column (25 x 1 cm) by NMR (Varian HA100) and mass spectrometry (Varian-Mat SM1-B).

Table I

| Physical data and yields of acetone acylals | | | |
|---|-------------|------------|-------|
| Compound | Bp | n_D^{20} | Yield |
| $(CH_3)_2C(OCOH)_2$ | 56°/16 mm | 1.4140 | 75% |
| $(CH_3)_2C(OCOCH_3)_2$ | 62°/25 mm | 1.4090 | 60% |
| $(CH_3)_2C(OCOCCL_3)_2$ | 110°/1.4 mm | (mp. 41°C) | 80% |
| $(CH_3)_2C(OCOCH_2Cl)_2$ | 116°/4.5 mm | 1.4475 | 75% |
| $(CH_3)_2C(OCOH)(OCOCH_2Cl)$ | 86°/5 mm | 1.4442 | 50% |

Preliminary results indicate that isopropenyl formate easily formylates weakly basic amino compounds. It seems especially valuable for formylations which are only possible in neutral medium. Investigations about a generalization of the synthetic method and reactivity of the compounds IV and V are in progress.

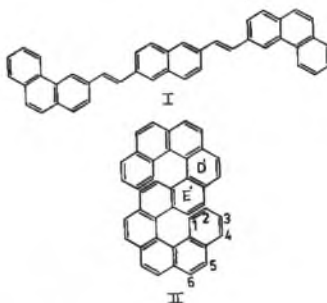
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accepted for publication in Rec.Trav.Chim. 1971.

SYNTHESIS OF A DOUBLE HELICENE¹⁾
RAC. AND MESO DIPHENANTHRO 3,4-c;3'4-l CHRYSENE

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(Received in UK 3 December 1970; accepted for publication 10 December 1970)

Photocyclization of 2,6-bis(3-phenanthrylethenyl) naphthalene (I) in benzene solution with added iodine affords among other products a double helicene (II).



Three stereo isomers, d, l and meso, are possible for II as pictured in fig.I. It is likely that the d and l structures in the conformation as drawn, possess a strong deformation of the aromatic rings in the middle part of the molecule, whereas the meso form has a more regular structure.

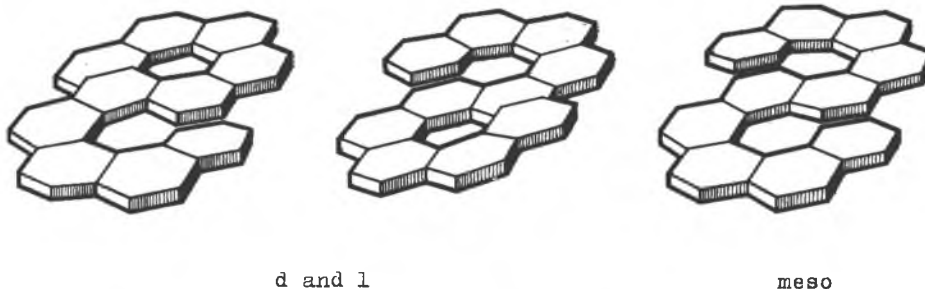


Fig.I The three possible structures of II

In fact two dehydrocyclization products (IIa and IIb) with identical U.V. and mass spectra ($M=528$) could be isolated.

IIa has mp.400-402° (from ethyl acetate).

IIb has mp.390° and is slightly soluble in most of the common organic solvents. Due to its low solubility the NMR spectrum of IIb (fig.II) could only be recorded in $AsCl_3$ solution by repeated scanning (36 times).

NMR spectra of IIa recorded in CDCl_3 (fig.II) and in AsCl_3 are very similar.

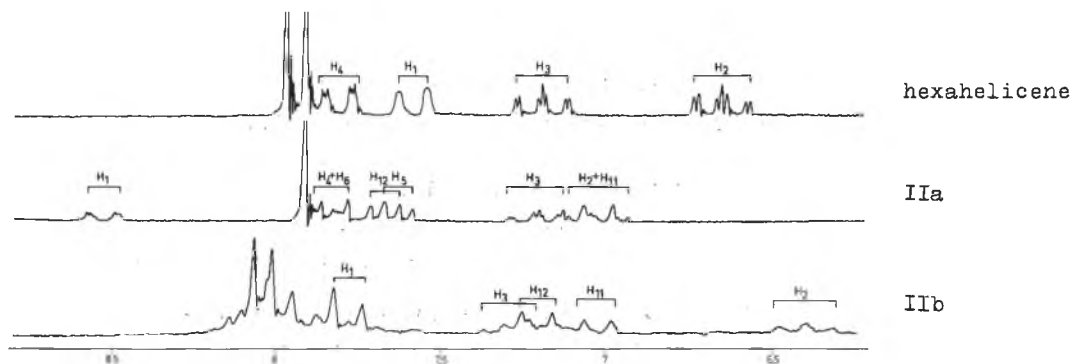


Fig.II NMR spectra of hexahelicene, IIa and IIb.

Comparison of the spectra of the isomers reveals some striking differences especially in the position of the protons H_1 and H_2 .

As expected proton H_2 in IIb has an upfield shift with respect to the equivalent proton in hexahelicene, due to the ring current of the nearby benzene ring D'. However, H_2 in IIa has been shifted in a downfield direction.

Proton H_1 in IIa has a very large downfield shift with respect to hexahelicene ($\Delta\delta=96$ cps). Obviously, H_1 in IIa does not experience the anisotropy of ring E', as has been found in all helicenes up till now. The same is true to a minor degree for H_2 in IIa. Another feature of the spectrum of IIa is that protons H_5 and H_6 have different chemical shifts contrary to the corresponding protons in hexahelicene and IIb.

A structure which might explain these facts is drawn in fig.III. In this structure the deformation expected in the centre of the molecule is shifted to the ends. As the torsion in the d and l forms must be larger than in the meso form we suppose IIa to have the asymmetric form, while IIb is the meso compound. Details of the synthesis of the compounds and of physical measurements will be given elsewhere in the near future.



Fig.III The proposed structure of IIa.

1) Part IV of Photodehydrocyclizations of stilbene-like compounds.